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Vol. I Applied Mechanics & Structural Engg., Civil Engineering, Water Resources Engg. & Mgmt., Architecture

Editor(s): Prof. Dhanesh Patel
Prof. U D Patel
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Strategy for reduction of Nitrate concentration in Groundwater by Analytical Hierarchy Process

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Abstract

Analytical Hierarchy Process (AHP) is decision-making tool to identify the most effective methods for reducing Nitrate concentrations in groundwater. Nitrate pollution is a serious problem, and it is essential to find ways to mitigate its effects on human health and the environment. The presence of excess Nitrate in drinking water can lead to diseases such as methemoglobinemia (blue baby syndrome). The study uses AHP to evaluate various methods of reducing Nitrate concentrations and rank them according to their effectiveness. The highest Nitrate concentration was observed at Maretha village in Vadodara city, where 232.8 mg/L of Nitrate was found in 26 groundwater samples taken from shallow and open wells. The AHP method of MCDA has been used to prioritize groundwater management strategies considering four criteria Primary Cost (PC), Operational Expenditure (OE), Reduction Time (RT) and Removal Efficiency (RE) and five remedial measures. The study also emphasizes the importance of stakeholder involvement and communication in implementing these measures. Overall, the study demonstrates the utility of AHP as a decision-making tool for addressing complex environmental problems. Agriculture is the main industry in the Northern area, so Pump and Fertilize (PAF) methods suitable. It is advised to use phytoremediation and PAF in the Western area, which is close to the Mahi Estuary and has valuable agricultural land. Due to the presence of sub-urban settlements and industrial zones, Pump And Treat (PAT) and Chemical Injection (CI) is the most appropriate method for treating the Central critical region.

Keywords: *Groundwater, Nitrate Contamination, Management Strategy, AHP*

1. Introduction

Humans depend on natural resources. The two main sources of water for household, agricultural and industrial uses are surface water and groundwater. One third of the world's population relies on groundwater for everyday requirements, primarily for drinking, due to a lack of surface water, especially in arid and semi-arid countries (Adimalla and Venkatayogi 2018). Apparently, the quality of groundwater is continuously declining due to anthropogenic impacts like industrial and agricultural operations as well as changes in the natural environment, which is leading to a water shortage crisis and numerous environmental issues. In the past 20 years, there have been many difficulties with groundwater contamination in the central Gujarat region. Aquifers have been contaminated by nitrate, fluoride, high salinity and effluent from industrial discharges (Krishnan S. et al. 2006).

The UV Spectro-photometric screening method has been used to determine Nitrate from the screening samples. Here 10 ml screened sample is taken and by adding distilled water a 50 ml solution is made, then 1 ml HCL is added before taking the absorption of samples. Then, Nitrate calibration curve (fig. 2) is prepared as per APHA (1998). The absorption values of each sample which have been taken with reference to stock Nitrate solution in photo-spectrometer, for the range of 220 nm and 275 nm from which the respective values of Nitrate concentration have been obtained.

Removing contaminated groundwater and recovering it to its original purity is the process of groundwater remediation. This can be done using either an ex-situ strategy, in which groundwater is to be removed by wells, treated on the surface and then placed back underground, or an in-situ approach, in which favourable circumstances are provided for the breakdown of pollutants into less dangerous products. According to King et al. (2012), there are two types of denitrification treatments: reduction technologies and removal technologies. The technologies for removing Nitrate include a number of physical, biological, and chemical processes. The concentrated waste streams or used adsorbents produced by these removal techniques are separately disposed of in physical processes. Moreover, the primary goal of biochemical activities is to convert Nitrate ions into other forms of nitrogen, such as ammonia or a more benign form like nitrogen gas (Archana et al. 2012). Because of their high unit costs and negative effects on the environment, traditional treatment techniques to control Nitrate problems in groundwater are expensive. An alternate strategy to Nitrate management based on in-situ bioremediation using the natural denitrifying potential of aquifers, may have a variety of advantages, including economic rewards and environmental sustainability (Tompkins et.al 2001, Soloman et.al 2018). For highly concentrated Nitrate plumes, the pump and treat approach is used to denitrify the area initially, before the Nitrate seeps further into the aquifer and disperses to affect a large area. If used on a large basin, this approach is less effective and more expensive.

The biological denitrification process and the chemical denitrification process are other Nitrate reduction techniques. Only certain microbes can break down and convert specific contaminants. Another limiting element is susceptibility to inhibition by hazardous pollutants like heavy metals (Hu et al., 2019). In-situ bioremediation is the process of degrading substances using either native or exogenous microorganisms by introducing microbial reagents and nutrients into groundwater (Juwarkar et al. 2010). Using microbial breakdown processes in sophisticated, regulated treatment systems is the basic idea behind bioremediation (Langwaldt et.al 2000). The most effective way of denitrification is biological denitrification, which is also the least expensive option because its effectiveness can approach 100% (Burghate et.al 2013). Efficiency is increased by a suitable environment; neutral pH is preferred, and temperatures below 5°C can prevent denitrification. Nevertheless, this approach requires more time years and maybe decades—and the second issue is aquifer biofouling (Tompkins et.al 2001).

Another effective approach for de-nitrifying groundwater is chemical denitrification, which is similarly quicker and less expensive. To prevent denitrification, it is necessary to maintain the ideal pH and temperature (Bei Zhao et. al. 2021). Even though, secondary contamination is a possibility and this treatment method's pH is a significant controlling factor. ZVI is typically utilised with materials based on iron (Zero valent iron). Permeable reactive barriers (PRBs) are a costly denitrification technique that work well at depths under 50 feet and sometimes up to 120 feet.

In the recent years, many researchers have focused on the sustainability of groundwater and the suitability of one remediation method over the others based on MCDA (multi criteria decision analysis) (An D et al 2015, An D et al 2016, Wang H. et al 2017, Li H et al 2019). An

D et al (2015 & 2016). These researchers used a combination of MCDA methods, such as Fuzzy-AHP-ELECTRE, and ranked the remediation alternatives PAT>AS>PRB>MNA; however, this study was not related to any specific contaminant but was instead more focused on the selection of criteria and their weighting. Four different MCDA techniques—WSM, WPM, CGT, and TOPSIS—were applied by Wang H et al. (2017) to 18 potential remediation approaches, with seven evaluation criteria considering contamination from oil wells in the Shengli oil fields under consideration. The purpose of this study is to provide remedial steps for Padra and Vadodara city, two central talukas of the Vadodara district. This included primary data collection of these two taluka in 2022 pre monsoon season. Another novelty of present research has focused on four fundamental criteria which are Primary Cost (PC), Operational Expenditure (OE), Remedial Time (RT) and Remedial Efficiency (RE) of five different remediation alternatives such as Phytoremediation (PHYTO), Pump And Treat (PAT), Pump And Fertilize (PAF), Permeable Reactive Barrier (PRB) and Chemical Injection (CI). The weights of criteria and remedial alternatives were optimised using the analytical hierarchy process (AHP) approach of MCDA, and the remedial alternative with the highest weight was recommended as the best groundwater management strategy.

The paper will be useful for policymakers to make decisions at the micro level and for the large scale implementation by state and central governments. The suggested remedial strategies can be verified by numerical simulation at the micro level (pilot level) for a particular well.

2. Materials and Methods

2.1 Study area characteristics:

The study area lies in Vadodara taluka in Gujarat District which has total 12 taluka. Out of these 12, two central talukas Vadodara and Padra have been chosen as the study area (Figure 1). The area of the alluvial region is about 1210 km2, residing between 72.50° to 73.20° eastern longitude and 22.00° to 22.30° northern latitude on a geographical basis. Mahi River, Vishwamitry River and Mini Drain are the three main surface water bodies in the study area. The general atmosphere of the study area is semi-arid with the highest temperature of 45° C in the summer and the lowest temperature of 8° C in the winter season and an average rainfall is 800-1000 mm in the central region of Vadodara district for the monsoon season. Groundwater is the major contributor for agricultural, industrial and domestic uses in the present research area. A cluster of small scale industries such as 33 miscellaneous chemical based industries, 41 process stone marbles industries, 64 chemical machinery parts producing units, 32 lather footwear producing units, etc., exist in study area (DIPS-Vadodara, 2016).

2.2 Ground Truth Study (GTS):

GTS is an important step which includes site exploration, primary data collection, sampling and laboratory testing of various physico-chemical groundwater parameters before opting for a suitable remediation method. The two principal talukas in the Central Vadodara region are Padra and Vadodara City. A total of 26 groundwater samples have been taken from openwells, shallow wells, and dug wells in the aquifer's unconfined zone. 11 of these 26 samples were taken from the Padra taluka, and the remaining 15 were taken from the Vadodara city taluka. According to APHA, the physico-chemical parameters were calculated, including pH, EC, Total Dissolved Solid (TDS), Nitrate, Fluoride, Chloride, Sulphate, Total Hardness (TH), Calcium, Magnesium, and Total Alkalinity at the. Fig 2 shows Nitrate absorbance curve for finding Nitrate concentration present in groundwater samples at Environment laboratory of the MSU Baroda. Fig 3 shows the sample location of groundwater in central region of Vadodara

District. Table 1 shows the results of the physico-chemical parameters of collected groundwater sample.

Figure 1 Critical region of Vadodara District

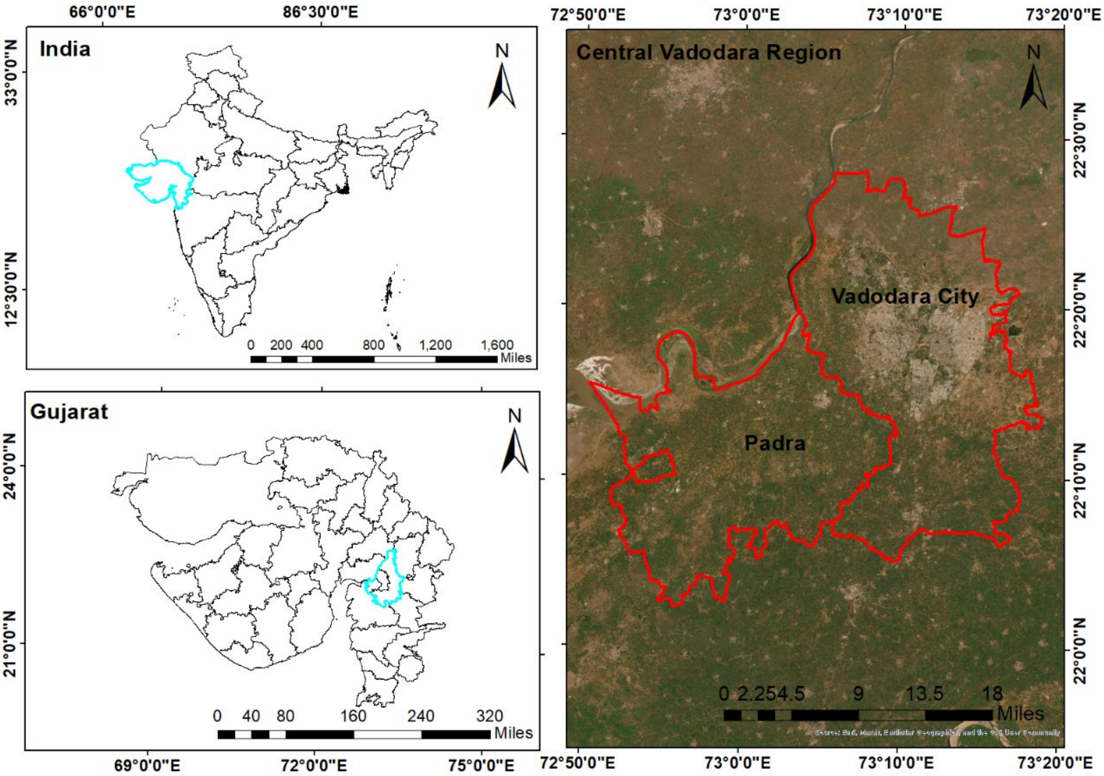


Figure 2 Nitrate absorbance curve

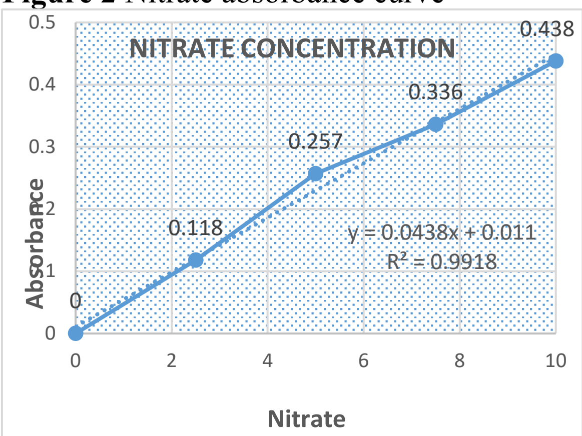
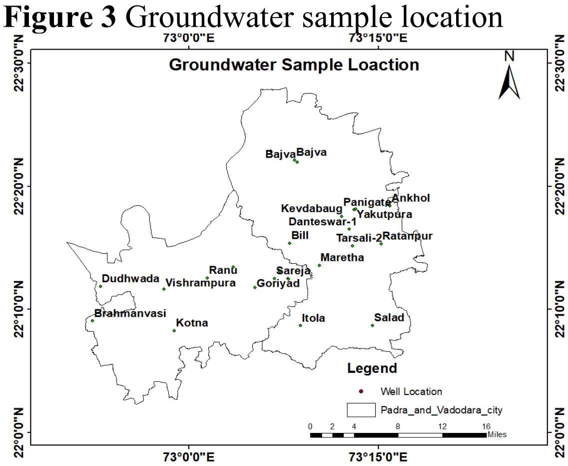


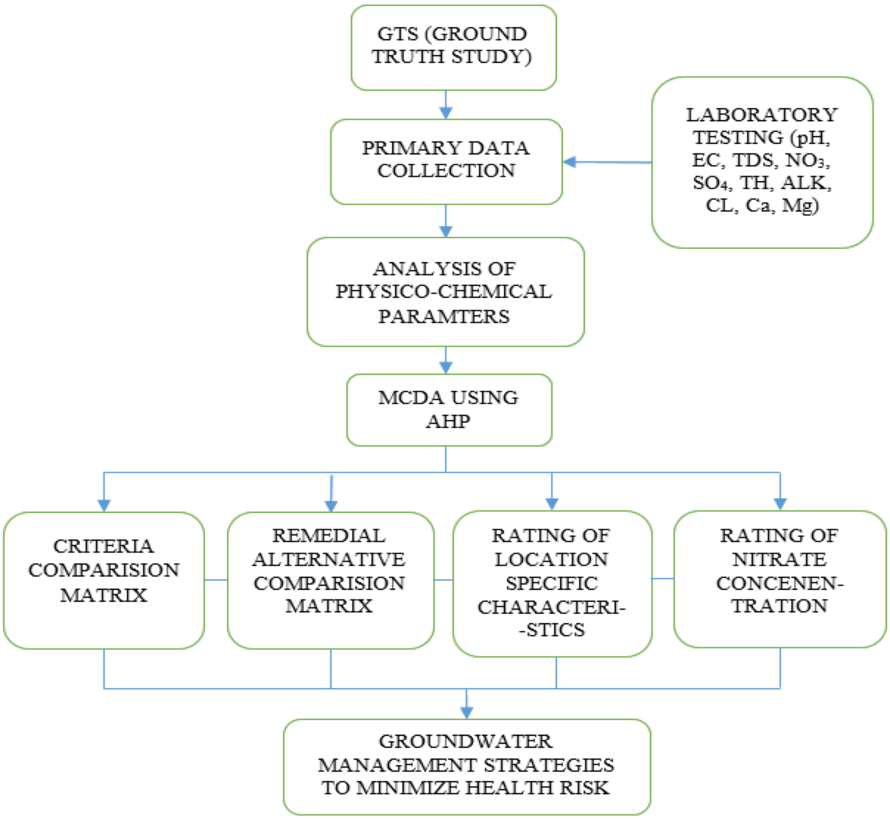
Figure 3 Groundwater sample location



2.3 Methods

Research work in this area takes a unique approach to assess the risk associated with groundwater remediation (figure-4). First step is Ground Truth Study (GTS) to understand the area specific characteristic, groundwater level, aquifer condition and water samples of the wells which has been present in unconfined zone of aquifer. Afterwards, these groundwater samples are tested in laboratory and analysed in accordance with Indian Standard 10500-2012. Last step is to suggest the best groundwater management strategies based on the Analytical Hierarchical Process of Multi Criteria Decision Making (MCDM) using the Rating of the Location Specific Characteristics (LSC) and the Nitrate concentration.

Figure 4 Methodological Flow Chart



2.3.1 Analytical Hierarchy Process (AHP)

The AHP first explained by Saaty (1980) is one of the most widely used MCDA methods that incorporates qualitative and quantitative data to reveal the choice orders of decision-makers (DMs). The starting step is to decompose the decision making problem in a hierarchical manner to develop the pairwise comparison matrix based on choice order of the alternatives (ranks) and criteria (weighs) considering from the inputs of DMs. A scale rating of nine orders in which 1 denotes equivalent and 9 indicates highest importance with 2 to 8 even numbers as intermediate ratings are assigned to each criteria and alternatives to compute weightage by following equation:

$$Pq = \lambda_{max} * q$$

Where, P is the comparison matrix of n dimension, λ_{max} is the highest eigenvalue of P and q is eigenvector corresponding to λ_{max}. The consistency of the comparison matrix has to be checked as the inputs from DMs might contradict their own preferences. The inclusion of consistency ratio (CR) in any MCDA method is a common practice to evaluate any inconsistencies in the comparison matrix.

$$CI = (\lambda_{max} - n)/ (n - 1)$$

$$CR = CI/RCI$$

Where CR is the consistency ratio, CI is the consistency index, RCI is the average random consistency index with the same dimension of the comparison matrix, n is the number of criteria/alternatives. If the CR is greater than 10%, the matrix is said to be inconsistent and DMs are advised to revise the matrix until CR comes below 10%.

Table 1 Primary data collection in central region of Vadodara

Sr.	Village	Lat	Long	Type of well	pH	EC	TDS	NO_3	F	Cl	SO_4	Ca	Mg	TH	ALK
1	Maretha	22.22617	73.17225	Shallow Well	6.55	1313	840	233	0.11	855	420	269	275	1800	490
2	Ankhol	22.30676	73.26512	Open well	7.19	5273	3375	101	0.12	695	473	192	148	1090	410
3	Bajva	22.36631	73.1429	Open well	8	1830	1171	128	0.4	315	31	92	83	570	420
4	Bajva	22.36886	73.13957	Open well	7.16	3231	2068	146	0.13	360	344	120	58	540	410
5	Bill	22.25644	73.13322	Hand pump	7.24	790	506	8	0.06	180	44	84	32	340	260
6	Danteswar-1	22.27525	73.21178	Open well	7.12	1524	975	7	0.02	270	142	88	51	430	460
7	Itola	22.14456	73.14731	Open well	7.82	846	541	16	0.1	150	40	52	58	370	290
8	Karchiya	22.38115	73.10838	Open well	7.32	1044	668	20	0.16	175	51	64	71	450	510
9	Kevdabaug	22.29278	73.20167	Hand pump	6.82	213	136	70	0.1	280	222	56	61	390	710
10	Panigate	22.30169	73.21781	Open well	7.71	1424	911	24	0.25	255	133	28	32	200	560
11	Patod-2	22.21846	73.12027	Open well	7.24	2035	1302	31	0.08	215	124	44	80	440	640
12	Ratanpur	22.25572	73.25349	Shallow Well	6.87	1304	835	43	0.08	315	36	100	73	550	380
13	Salad	22.14503	73.24252	Shallow Well	7.26	3183	2037	1	0.04	175	24	40	75	410	560
14	Tarsali-2	22.25258	73.21608	Open well	7.4	310	198	14	0.13	240	71	156	49	590	340
15	Yakutpura	22.30267	73.21986	Open well	7.4	1773	1135	5	0.2	290	184	24	41	230	630
16	Chansad-1	22.20861	73.13111	Open well	8.15	280	179	111	0.11	535	147	44	68	390	780
17	Chansad-2	22.20778	73.13164	Open well	7.54	205	131	96	0.13	405	42	92	71	520	510
18	Patod-1	22.21925	73.11967	Hand pump	8.13	1980	1267	1	0.01	125	64	36	41	260	300
19	Sareja	22.20822	73.11325	Open well	7.53	300	192	27	0.12	525	51	44	95	500	160
20	Kotna	22.1377	72.9813	Shallow Well	7.86	2616	1674	70	0.44	964	94	131	112	800	348
21	Latipura	22.22408	73.05846	Shallow Well	8.45	952	609	73	0.91	132	44	70	68	460	556
22	Vishrampura	22.19409	72.96771	Shallow Well	7.96	2194	1404	104	1.32	448	118	185	156	1108	816
23	Brahmanvasi	22.15103	72.87352	Shallow Well	8.03	828	530	16	2.49	120	12	19	24	148	556
24	Dudhwada	22.19749	72.88378	Shallow Well	8.08	2552	1633	3	1.62	992	76	121	114	780	492
25	Goriyad	22.19586	73.08733	Shallow Well	7.99	1286	823	34	0.98	344	32	42	46	300	600
26	Ranu	22.20925	73.02487	Shallow Well	8.4	1246	797	33	2.78	280	22	35	36	240	668

3. Results and Discussions

Groundwater Nitrate concentrations obtained from primary data collection of Vadodara city and Padra taluka of Vadodara district (26 water sample of 2022 of Pre-monsoon season) was used to develop spatial distribution maps for pre seasons in GIS environment (IDW-Interpolation) to visualize areas with high contamination. From the Table 1 which shows the results of collected water samples and indicate the 10 wells out of the 26 wells, Nitrate concentration above 45 mg/L. From these maps (Figures: 4), only the blue and grey zone indicates area where Nitrate contamination is below Indian standards, everywhere else they are above the Indian standards.

The highest Nitrate contamination is found in certain pockets of central regions. The lowest observed Nitrate concentrations are in the range of 1 mg/L in Patod block in Padra pre monsoon seasons whereas highest concentrations are in the range of 232.8 mg/L in Maretha block of Vadodara city for pre monsoon seasons respectively. As per the Ground Truth Study (GTS), Both Padra and Vadodara city talukas are highly dominated by industrial and agricultural activities. These map were further utilized in identified the area distribution of the Nitrate concentration in the study area. Classification of area is distributed into five classes 1 to 15, 15.1 – 45, 45.1 – 90, 90.1 – 150 and 150.1 – 232.8. The Area distribution of Nitrate concentration in study area is shown in table-2 which indicate only 29 % of the area is below the permissible limit remaining 71% area is above permissible limit

Figure 4 Nitrate concentration in study area

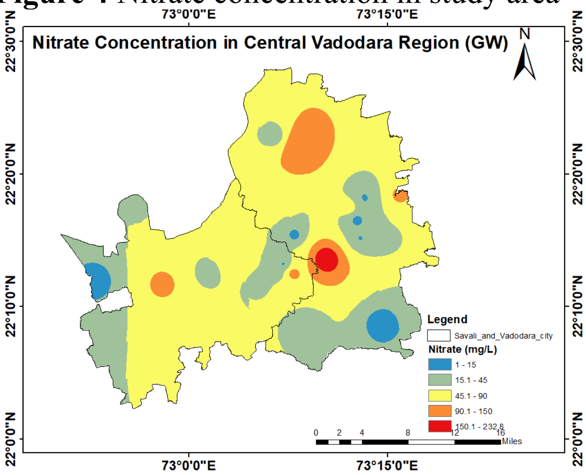


Table 2 Area distribution of Nitrate

SR No.	Classification (mg/L)	Area (Km^2)	Percentage Area (%)
1	1 - 15	30.45	2.51
2	15.1 – 45	320.67	26.43
3	45.1 - 90	774.37	63.83
4	90.1 - 150	79.72	6.57
5	150 – 232.8	8.01	0.66

The highest eigenvalue (λmax) of the criteria comparison matrix (Table-3) is 4.26, the consistency index (CI) is 0.09, the average random consistency index (RCI) of four criteria is 0.9 given in Table-4 and submitting above values in equation (4) and (5), the consistency ratio (CR) is found to be 9.69% which is less than 10% making the comparison matrix to be consistence. The same AHP method was applied to evaluate alternatives for each criteria mentioned in Table-5, 6, 7 and 8 representing remediation alternatives comparison matrix for Primary Cost (PC), Operational Expenditure (OE), Remediation Time (RT) and Remediation Efficiency (RE) respectively. The weights obtained for each criteria and each remedial alternative per criteria have been termed as local weights mentioned in Table-9.

The product of local weights of respective criteria and alternatives have been termed as global weights which helped in determining the choice order of remedial measures based on sorting values from high to low highlighting the descending preferential sequence as (1) PAT (2) CI (3) PRB (4) PAF (5) PHYTO. A single well has been calculated at a time using this method, for example, well no. 1 (Maretha, Vadodara city) calculation presented in this paper. Such choice order was then applied at each primary well location falling in the critical area with Nitrate concentration above permissible limit and respective location specific characteristics (LSC).

A rating has been assigned based on the primary data collection of Nitrate concentration and location-specific characteristics shown in table 10 and 11. A maximum rating is assigned to Nitrate concentration greater than 150 mg/l and Urban highly population area, improper sewerage which is 5. Low rating of Nitrate, LSC have been matched with low-ranking remediation methods obtained from MCDA-AHP. Based on table 12 which is shows the Nitrate concentration from primary data collection, sample location specific characteristics and suitable remedial strategy for each well, which has more than the permissible limit (> 45mg/L).

Table 3 Criteria comparison matrix

Criteria	PC	OE	RT	RE
PC	1	2	0.25	0.20
OE	0.5	1	0.25	0.33
RT	4	4	1	0.5
RE	5	3	2	1

Table 4 Random consistency index RCI

n	1	2	3	4	5
RCI	0	0	0.58	0.9	1.12
n	**6**	**7**	**8**	**9**	**10**
RCI	1.24	1.32	1.41	1.45	1.49

Table 5 Matrix for Primary Cost

PC	PHYTO	PAT	PAF	PRB	CI
PHYTO	1	5	0.5	4	3
PAT	0.2	1	0.2	0.5	0.33
PAF	2	5	1	4	3
PRB	0.25	2	0.25	1	0.5
CI	0.33	3	0.33	2	1

Table 6 Matrix for Operational Expenditure

OE	PHYTO	PAT	PAF	PRB	CI
PHYTO	1	2	0.25	0.5	0.33
PAT	0.5	1	0.2	0.33	0.25
PAF	4	5	1	3	2
PRB	2	3	0.33	1	0.5
CI	3	4	0.5	2	1

Table 7 Matrix for Remediation Time

RT	PHYTO	PAT	PAF	PRB	CI
PHYTO	1	0.2	0.5	0.33	0.25
PAT	5	1	4	3	2
PAF	2	0.25	1	0.5	0.33
PRB	3	0.33	2	1	0.5
CI	4	0.5	3	2	1

Table 8 Matrix for Remediation Efficiency

RE	PHYTO	PAT	PAF	PRB	CI
PHYTO	1	0.25	2	0.5	0.33
PAT	4	1	5	3	2
PAF	0.5	0.2	1	0.33	0.25
PRB	2	0.33	3	1	0.5
CI	3	0.5	4	2	1

Table 9 Weights of criteria and alternatives from AHP

Criteria	Criteria	Local weights of alternatives					Global weights of alternatives				
	Weights	PHYTO	PAT	PAF	PRB	CI	PHYTO	PAT	PAF	PRB	CI
PC	0.12	0.31	0.06	0.40	0.09	0.14	0.035	0.007	0.047	0.010	0.017
OE	0.10	0.10	0.06	0.42	0.16	0.26	0.009	0.006	0.040	0.015	0.025
RT	0.33	0.06	0.42	0.10	0.16	0.26	0.020	0.137	0.032	0.053	0.086
RE	0.46	0.10	0.42	0.06	0.16	0.26	0.045	0.191	0.029	0.074	0.120
Total	1.00	0.56	0.95	0.98	0.57	0.93	0.111	0.341	0.148	0.153	0.248

Table 10 Nitrate Range Rating

Nitrate (mg/l)	Rating
1 – 15	1
15.1 – 45	2
45.1 – 90	3
90.1 – 150	4
150+	5

Table 11 LSC Criteria Rating

LSC (Location Specific Characteristics)	Rating
Rural area, agricultural activities	1
Agricultural activities, soak pits leachate, Faulty sewerage	2
Rural area, agricultural, sea water intrusion	3
Industrial effluents, agricultural activities	4
Urban highly population area, improper sewerage	5

Table 12 Groundwater Nitrate from primary data collection and location specific characteristics

Sr.	Village	Location	LSC: Location Specific Characteristics	NO_3 (mg/l)	(NO_3) Range Rating	(LSC) Criteria Rating	Suitable Remedial Strategy
W1	Maretha	Hand Pump, Rabari Vas	Agricultural activities, soak pits leachate, Faulty sewerage	233	5	2	PAT
W2	Ankhol	OW Nr. ESR	Rural area, agricultural activities improper sewerage	101	4	2	PHYTO
W3	Bajva	OW Nr. railway line, bajva	Agricultural activities, soak pits leachate, Faulty sewerage	128	4	2	PAF
W4	Bajva	OW Nr Kaushalya Vardhankendra	Agricultural activities, soak pits leachate, Faulty sewerage	146	4	2	PAF
W9	Kevdabaug	Bethak mandir, kevdabaug	Urban highly population area, improper sewerage	70	3	5	CI
W16	Chansad-1	Opposite BAPS mandir	Rural area, agricultural activities, soak pits leachate	111	4	1	PAF
W17	Chansad-2	Opposite panchayat karyalay	Rural area, agricultural activities, soak pits leachate	96	4	1	PAF
W20	Kotna	Well Kotna headworks	Industrial effluents, agricultural activities	70	3	4	PAT
W21	Latipura	Hand Pump In Primary School	Urban highly population area, improper sewerage	73	3	5	PRB
W22	Vishrampura	Open Well ANANDPURA	Rural area, agricultural activities, soak pits leachate	104	4	3	PHYTO

4. Conclusions

This study revealed high Nitrate in groundwater of the central region of Vadodara namely, Vadodara city and Padra city. In this study, Primary data of 26 locations for pre monsoon season has been collected and tested in laboratory. The result indicated the NO3 in the groundwater ranges from 1mg/l (Patod Village, Padra) to 232.8 mg/l (Merath Village, Vadodara city).

As per the observations of Ground Truth Study, different anthropogenic activities are the prime sources of high Nitrate i.e., agricultural activities, industrial activities, leaching from soak-pits, etc. Based on four fundamental criteria, such as the Primary Cost (PC), Operational Expenditure (OE), Remediation Time (RT) and Remediation Efficiency (RE), AHP identified the most effective remedial measures in descending order for well no. 1 (Maretha, Vadodara city) (1) PAT (2) CI (3) PRB (4) PAF (5) PHYTO. For all wells with more than their permissible limit, the same calculation was carried out.

The location specific characteristics (LSC) such as rural area, agricultural activities, lack of drainage of sewers, animal husbandry, etc. has further helped in assigning the remedial measures to each well location that showed Nitrate contamination above permissible limit. In the Northern region, majority of population is involved in agricultural activities, and there are some industries nearby Bajwa village area thus the use of Pump and Fertilize (PAF) and Phytoremediation methods for denitrification are the most suitable methods.

In the Western region, the population is involved in agricultural activities and there are other sources of Nitrate injection in groundwater i.e., rural sanitation consisting of soak pits thus Phytoremediation, Pump and Fertilize (PAF) and Permeable Reactive Barrier (PRB) are the recommended methods for denitrification. The Central region consists industrial area and urban area of Vadodara city Maretha village having high density population thus Pump and Treat (PAT) method is suggested for denitrification of groundwater. To increase the efficiency of Pump and Treat (PAT) method for denitrification purpose the cost-benefit analysis is required.

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